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NORADAMANTANE AND NORADAMANTAN-9-ONE FROM TRANSANNULAR CARBENE INSERTION REACTIONS

M.R. Vegar and R.J. Wells

Department of Chemistry, University College of Townsville,
Queensland, Australia.

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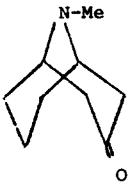
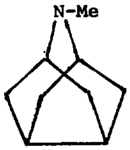
A recent note(1) reporting the conversion of pseudo pelletierine (I) to N-methyl-9-azatricyclo [3.3.1.0$^{3.7}$] nonane (II) by transannular 3,7 insertion of a carbene intermediate prompts us to record the results of a similar approach in the bicyclo [3.3.1] nonane series



I



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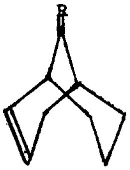
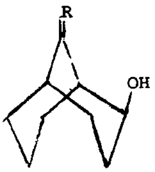


III R = O

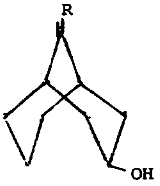
IV R = -O-CH$_2$
|
-O-CH$_2$

V R = H$_2$



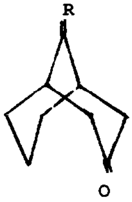
VI R = H$_2$

VIII R = -O-CH$_2$
|
-O-CH$_2$



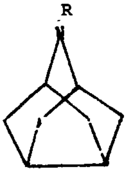
VII R = H$_2$

IX R = -O-CH$_2$
|
-O-CH$_2$



X R = H$_2$

XI R = -O-CH$_2$
|
-O-CH$_2$



XII R = H$_2$

XIII R = -O-CH$_2$
|
-O-CH$_2$

XIV R = O

XV R = H, OH

The aim of this work has been the synthesis of functionalised isoadamantanes by transannular carbene insertion of suitably protected bicyclo [4.3.1] decan-3-ones. The ready availability(2) of bicyclo [3.3.1] non-2-en-9-one (III) led us to test the general feasibility of such an approach by the preparation of noradamantane derivatives.

Carbena-cyclooctane has been reported(3) to form products resulting from 1,2 insertion; 1,3 insertion and transannular 1,5 insertion in the ratio 5:1:5. A study of models indicated that 1,3 insertion of a 3-carbena bicyclo [3.3.1] nonane would be very unlikely if the bicyclononane system adopted the favoured chair-chair conformation(4) during reaction. We were, therefore, confident that only two products, olefin and noradamantane, would result from insertion reactions of 3-carbena bicyclo [3.3.1] nonanes and that suitably protected substituents at position 9- would not hinder the reaction.

Bicyclo [3.3.1] non-2-en-9-one (III) was converted to the olefin (IV) in 60% yield by distillation of its semicarbazone with dry powdered potassium hydroxide. Hydroboration of (V) with a diborane: olefin ratio of 2:1 gave a high yield of a mixture of bicyclo [3.3.1] nonan-exo-2-ol (VI) and bicyclo [3.3.1] nonan-exo-3-ol (VII). Hydroboration of the olefinic ketal (IV) produced a similar ratio of the corresponding exo-2- and exo-3 alcohols (VIII& IX). In each case the exo-3-alcohol represented 66% of the mixture and could be separated from the exo-2-ol by chromatography on alumina. The structural assignments for alcohols (VIII) & (IX) followed from the observation of strong intramolecular hydrogen bonding in the I.R. spectrum of (VIII) not present in (IX).

Both exo-3-alcohols (VII) and (IX) were oxidised with Jones reagent to give almost quantitative yields of the corresponding ketones (X) and (XI) and thence converted to their tosylhydrazones.

The sodium salt of each tosylhydrazone was prepared by reaction with sodium methoxide in methanol, followed by removal of the solvent at low temperature. In preparative runs the dry salt was pyrolysed at 150-180° thus avoiding the troublesome separation of products from solvent. The thermal decomposition of the tosylhydrazone salt of (X) was also studied in diglyme.

Dry pyrolysis of the tosylhydrazone salt of (X) gave better than 90% of a mixture containing olefin (V) (35%) and noradamantane (XII) (65%). Gas chromatographic analysis of the mixture of olefin-noradamantane was carried out on a column containing 10% of a 3:1 mixture of diethylene glycol succinate and silver perchlorate.* The same olefin-noradamantane ratio was obtained in diglyme. It is interesting to note that in the pseudo pelletierine series(1) exclusive formation of the 3:7 insertion product was obtained, with no olefin production, when the tosylhydrazone salt of (I) was decomposed in diglyme.

The separation of (V) and (XII) was readily achieved by chromatography on silica gel-silver nitrate giving noradamantane m.p. 203° and undepressed on admixture with an authentic specimen.

The tosylhydrazone salt of (XI) gave a 35% yield of a mixture of (IV) and the ethylene ketal of noradamantan-9-one (XIII) containing 60% of (XIII). Separation of the mixture by preparative g.l.c. on a Carbowax 20 M column at 170° gave (XIII) as colourless plates m.p. 52-53°. Acid catalysed hydrolysis of (XIII) in aqueous methanol gave the parent ketone (XIV)(m.p. 193-195°) which could be converted to the parent hydrocarbon by Wolff-Kishner reduction. Noradamantan-9-ol (XV) (m.p. 244-7°) was prepared by reduction of the ketone with sodium borohydride.

These results and those of the Japanese workers' demonstrate that transannular carbene insertion reactions may be used to synthesise functionalised polycyclic ring systems which would be difficult to prepare by other methods. Work is now in progress on the synthesis of functionalised isoadamantanes.

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*We have found that silver perchlorate is readily soluble in a variety of polyester and polyglycol stationary phases. In the work reported above and in related work on the thermal decomposition of the salt of bicyclo [3.3.1] nonan-9-one tosylhydrazone excellent separations of olefins have been obtained on a polyester-silver perchlorate phase. This phase has satisfactory thermal stability at 100° and may also be used in the selective separation of olefins and arenes.

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